X-rays and Neutrons for Directed and Self-Assembly

Eric W. Kaler

Department of Chemical Engineering
University of Delaware
Newark, DE 19716

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Overview

- Self-Assembly Characterization
- Chemical Transformation - Polymerization
- External Field - Rheology and Flow Alignment

- SANS Method
  - Isotope variation (H and D) to provide contrast

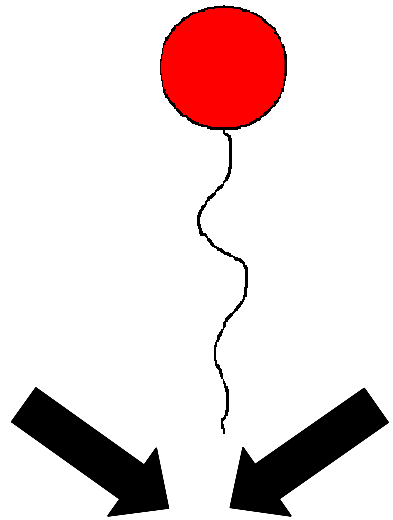
Aqueous Surfactants

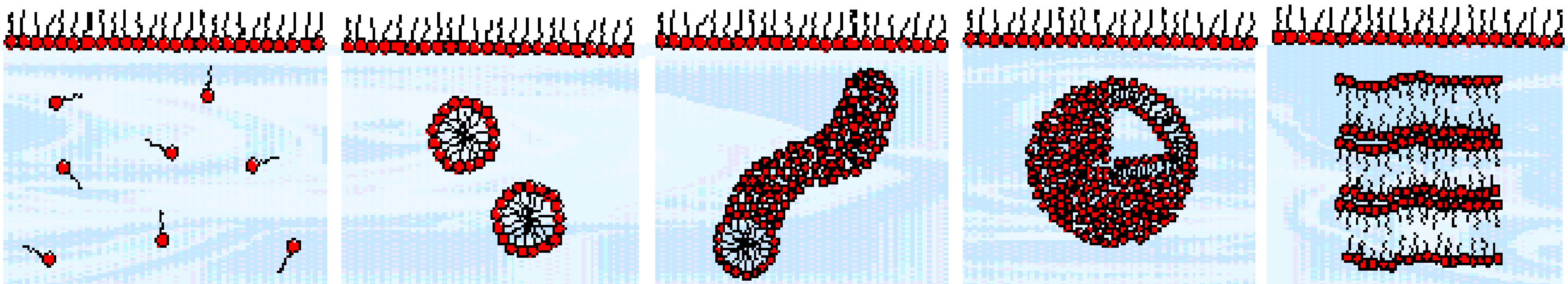
<u>Surfactant structure</u>

- Hydrophilic Head Group
- Hydrophobic Tail
- Counterion

<u>Solution Conditions</u>

- Temperature
- Concentration
- Salts
- pH
- Additional Molecules
  – ex. Hydrotropes





Monomers | Micelles | Elongated Micelles | Vesicle | Lamellar

Macroscopic Properties

•Surface Tension

•Viscosity

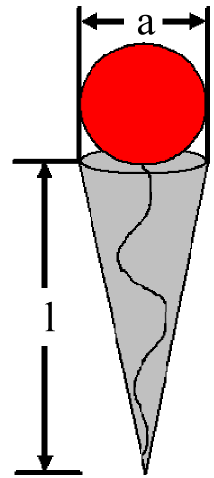
•Solubility

Aqueous Surfactants

Packing Parameter

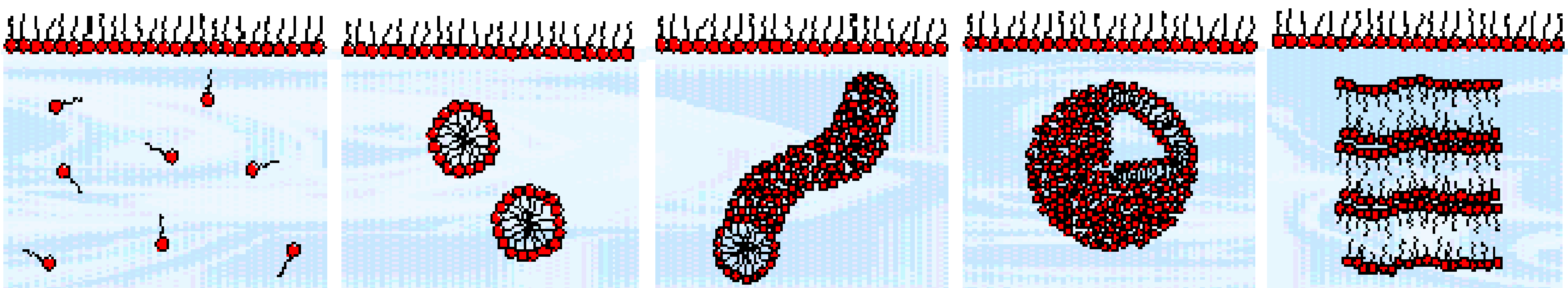
$$P = \frac{v}{al}$$

- a – Head group cross-sectional area
- l – Length of tail
- v – Volume of tail



Solution Conditions

- Temperature
- Concentration
- Salts
- pH
- Additional Molecules
  - ex. Hydrotropes



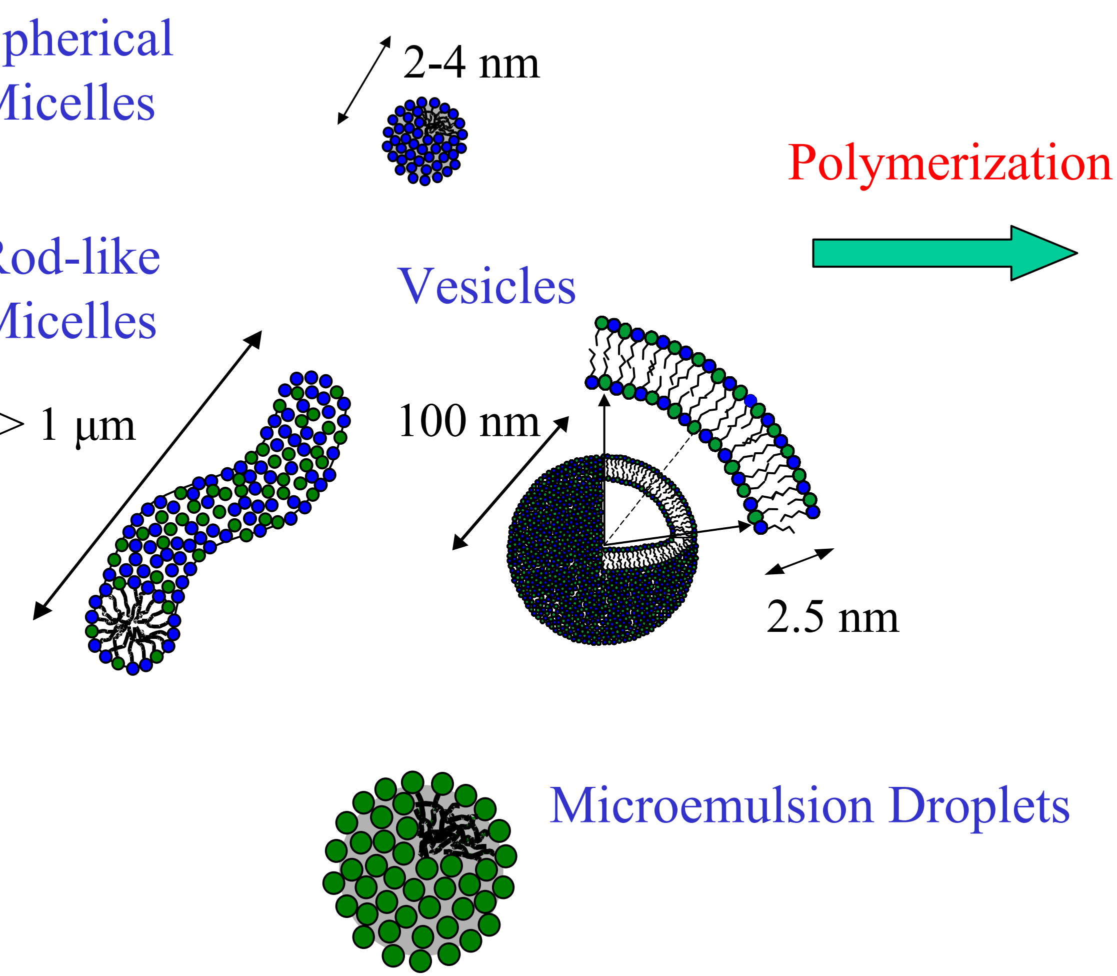
Monomers | Micelles | Elongated Micelles | Vesicle | Lamellar

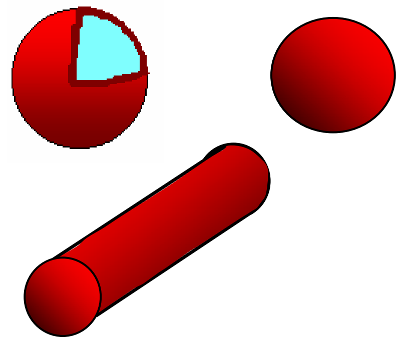
$$\mathbf{P} \longrightarrow \leq \frac{1}{3} \longrightarrow \leq \frac{1}{2} \longrightarrow \leq 1 \longrightarrow \approx 1$$

Macroscopic Properties

- Surface Tension
- Viscosity
- Solubility

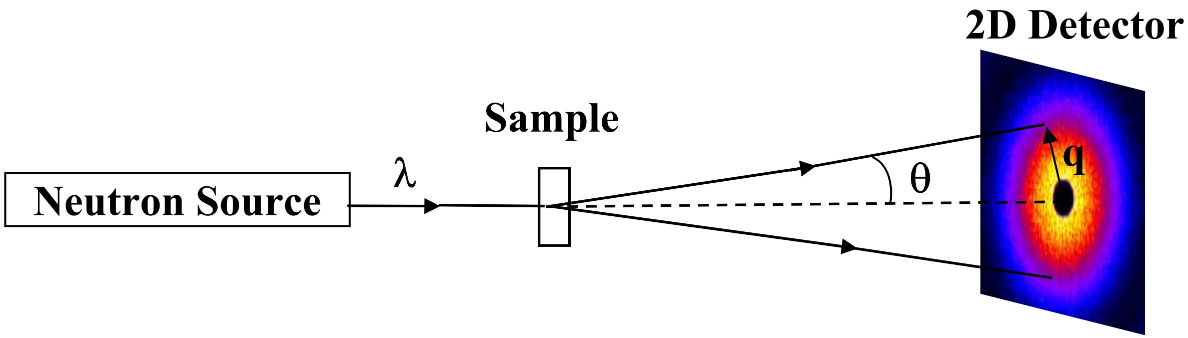
Self-organized surfactant solutions: promising tool for the templated (directed) synthesis of organic and inorganic materials





- Increased strength
- Stability to solution condition
- Capture aggregate dimension

Small Angle Neutron Scattering (SANS)



$$q = \frac{4\pi}{\lambda}\sin\left[\frac{\theta}{2}\right] \qquad q \sim \frac{1}{\text{Length}}$$

$$I(q) = n\, P(q)\, S(q)$$

$P(q) \Rightarrow$ Form Factor $\Rightarrow$ Single particle properties (size, shape, composition)

$S(q) \Rightarrow$ Structure Factor $\Rightarrow$ Relative positions of particles due to interactions

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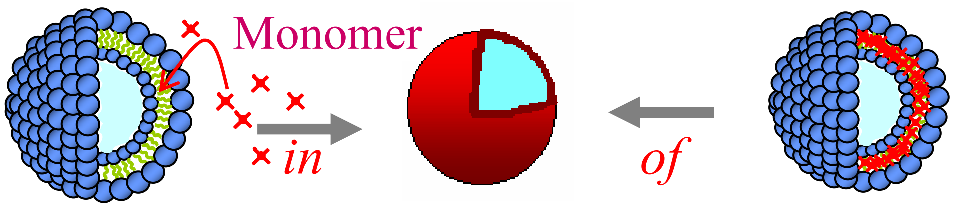
NIST

Vesicle Templating



McKelvey *et al. Langmuir,* **2000** Liu *et al. Langmuir,* **2003**

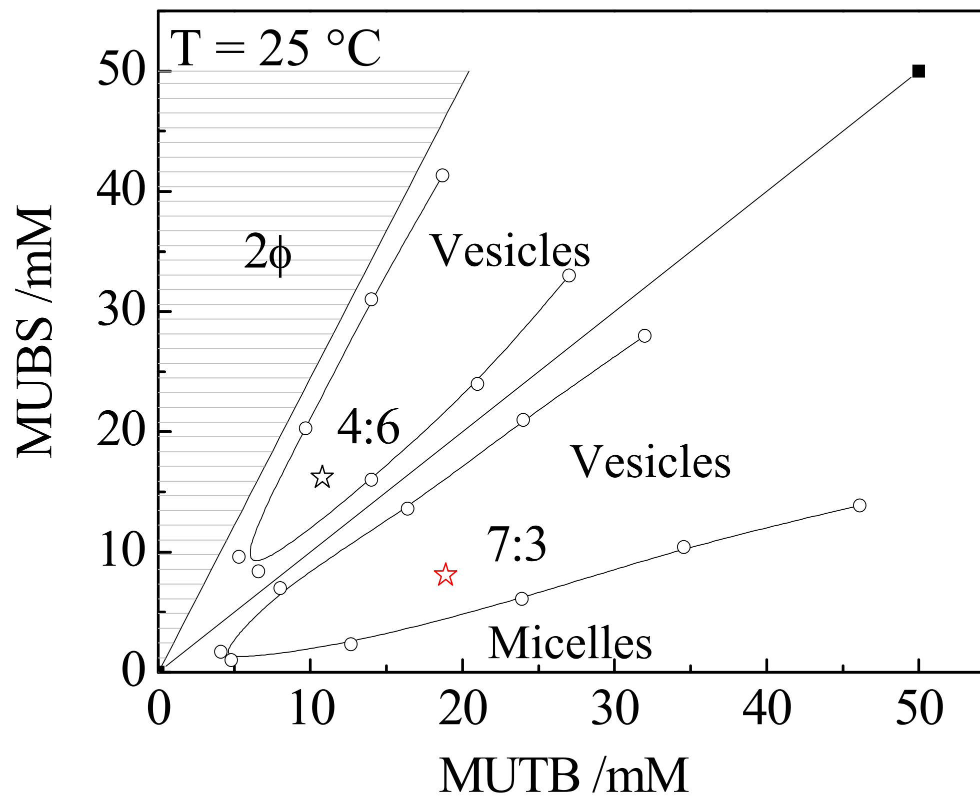
- Polymerization *in* or *of* vesicles allows replication of their architecture

- Fixation of vesicles (*of*):

Methacryloyloxyundecyltrimethyl ammonium bromide (MUTB)

Polymerizable surfactants

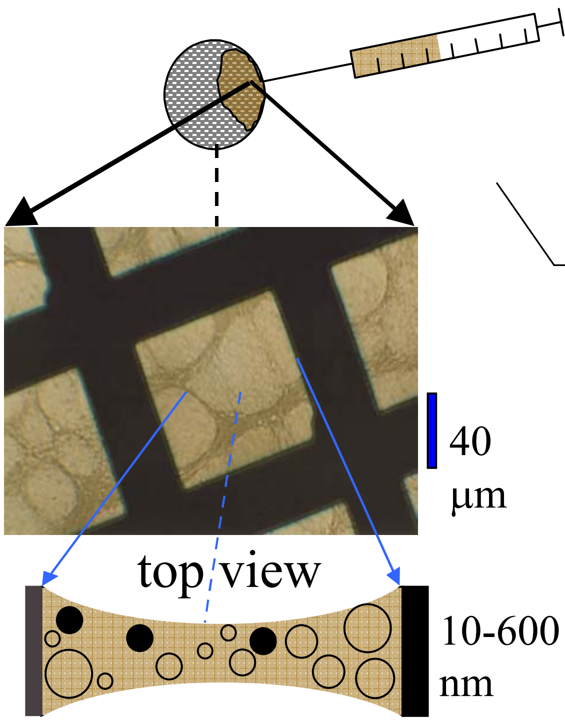
Sodium 4-ω-methacryloyloxyundecyl) oxybenzene sulfonate (MUBS)



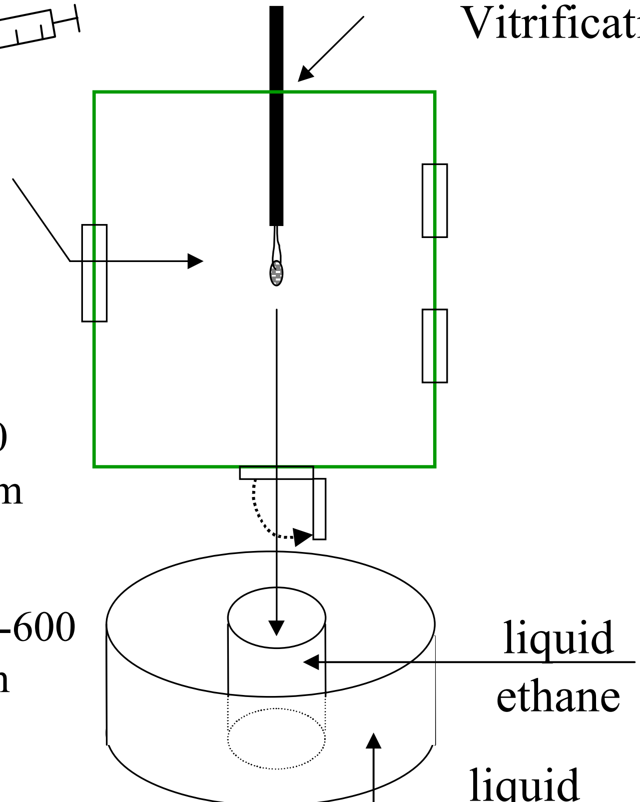
Cryogenic Transmission Microscopy (cryo-TEM)

Sample preparation goal: lock in microstructure by rapid cooling

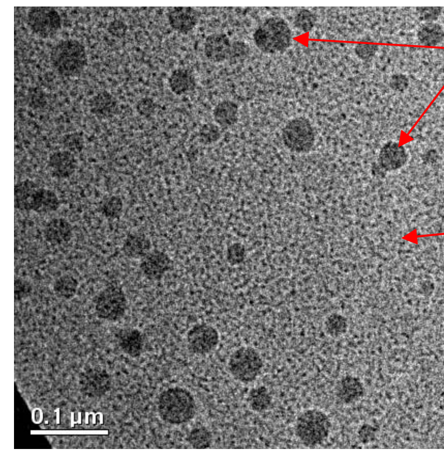
1. holey carbon grid

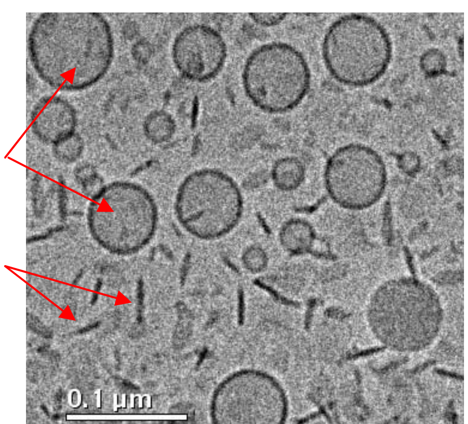


2. CEVS => Controlled Environment Vitrification System



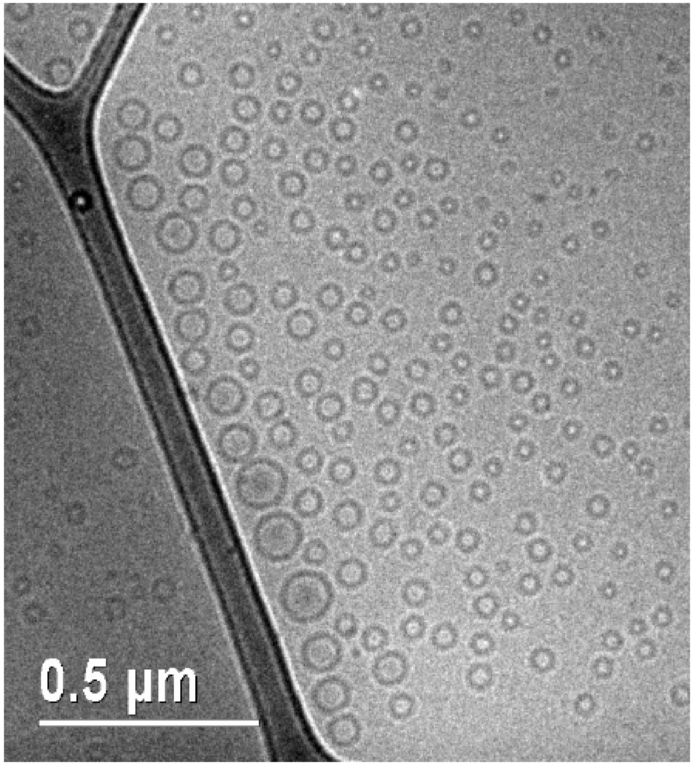
3. TEM imaging: 100 keV



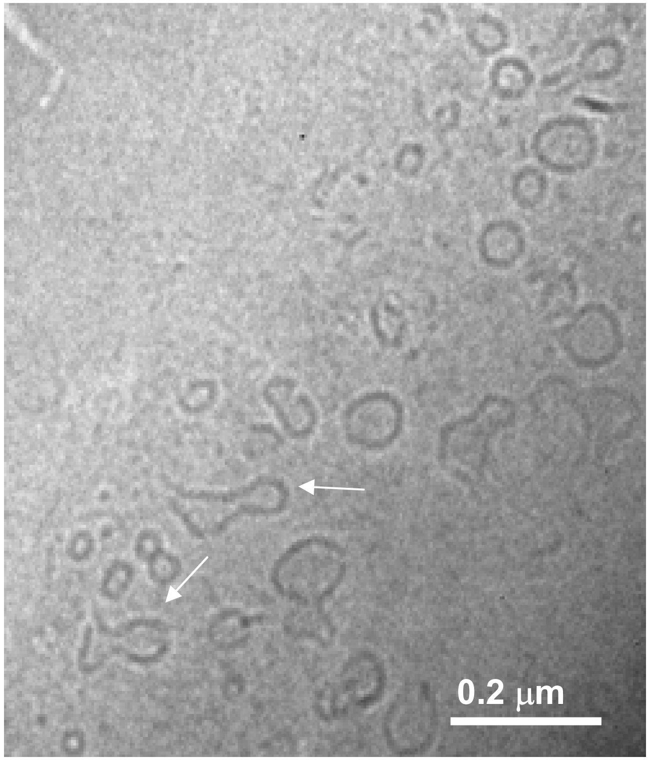


CTAB-FC_7 and
IR-400 mixture

Cryo-TEM of Polymerizable Vesicles



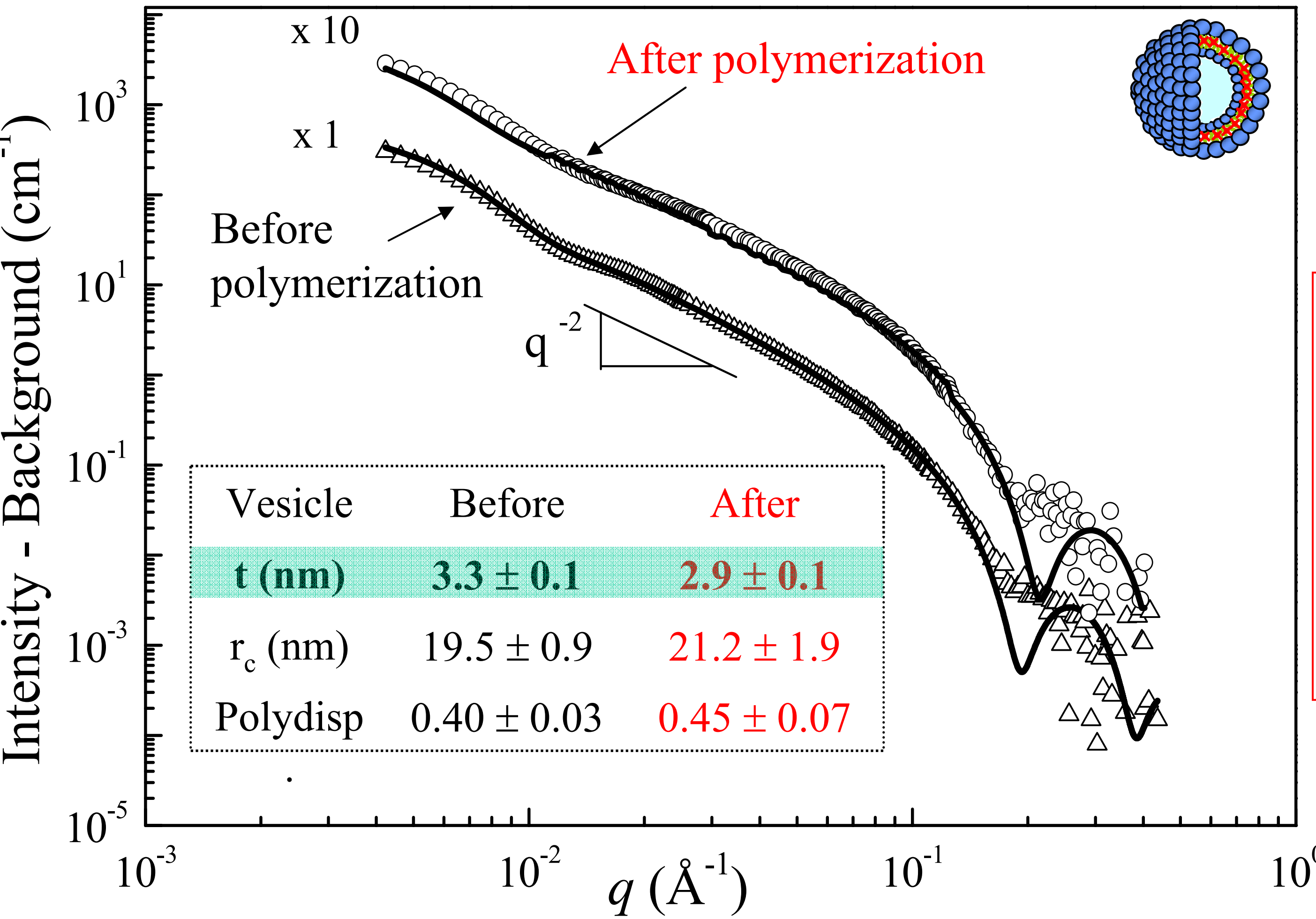
Before polymerization; QLS = 98 nm



After polymerization; QLS = 100 nm

- Size of the polymerized vesicles is comparable to that of the original vesicles
- A mixed population of spherical and irregular shaped unilamellar vesicles
- Complex morphology could be caused from the use of ionic initiator or from the reaction process

SANS Spectra of Polymerizable Vesicles



Vesicle	Before	After
t (nm)	**3.3 ± 0.1**	**2.9 ± 0.1**
r_c (nm)	19.5 ± 0.9	21.2 ± 1.9
Polydisp	0.40 ± 0.03	0.45 ± 0.07

$$I(q) = n\,P(q)\,S(q)$$

Model of P(q):

- Polydisperse-core-she

- Schulz distribution

- Minimized χ^2

- Bilayer thickness reduction due to polymerization of double bonds
- Polymerized vesicles appear to be a replica of the original vesicles

SANS Characterization

- Determination of nano-scale self assembly dimensions and interactions
- Polymerization can capture structures

- Contrast variation can isolate properties

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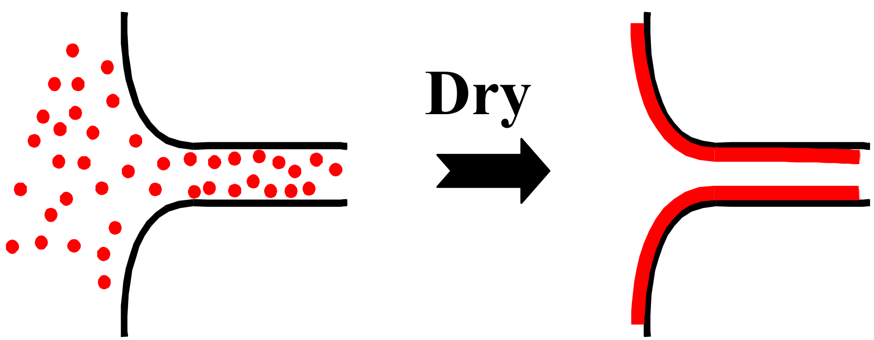
Why Study Microemulsion Polymerization?

Produces nanosized (~15 nm) latex particles smaller than those obtainable by emulsion polymerization

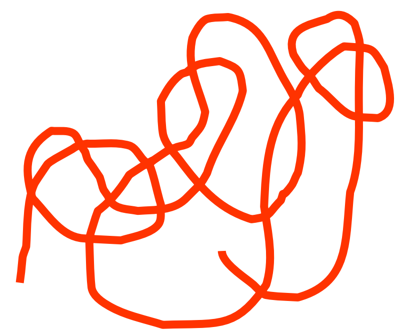
“Paint” the walls of a microporous material



“Seeds” for emulsion polymerization

Polymerization in a confined environment may lead to unique polymer morphologies, e.g. tacticity and knotting.

“Knotted” polymer chain in solution



Extremely high MW (~20 million daltons) are readily made

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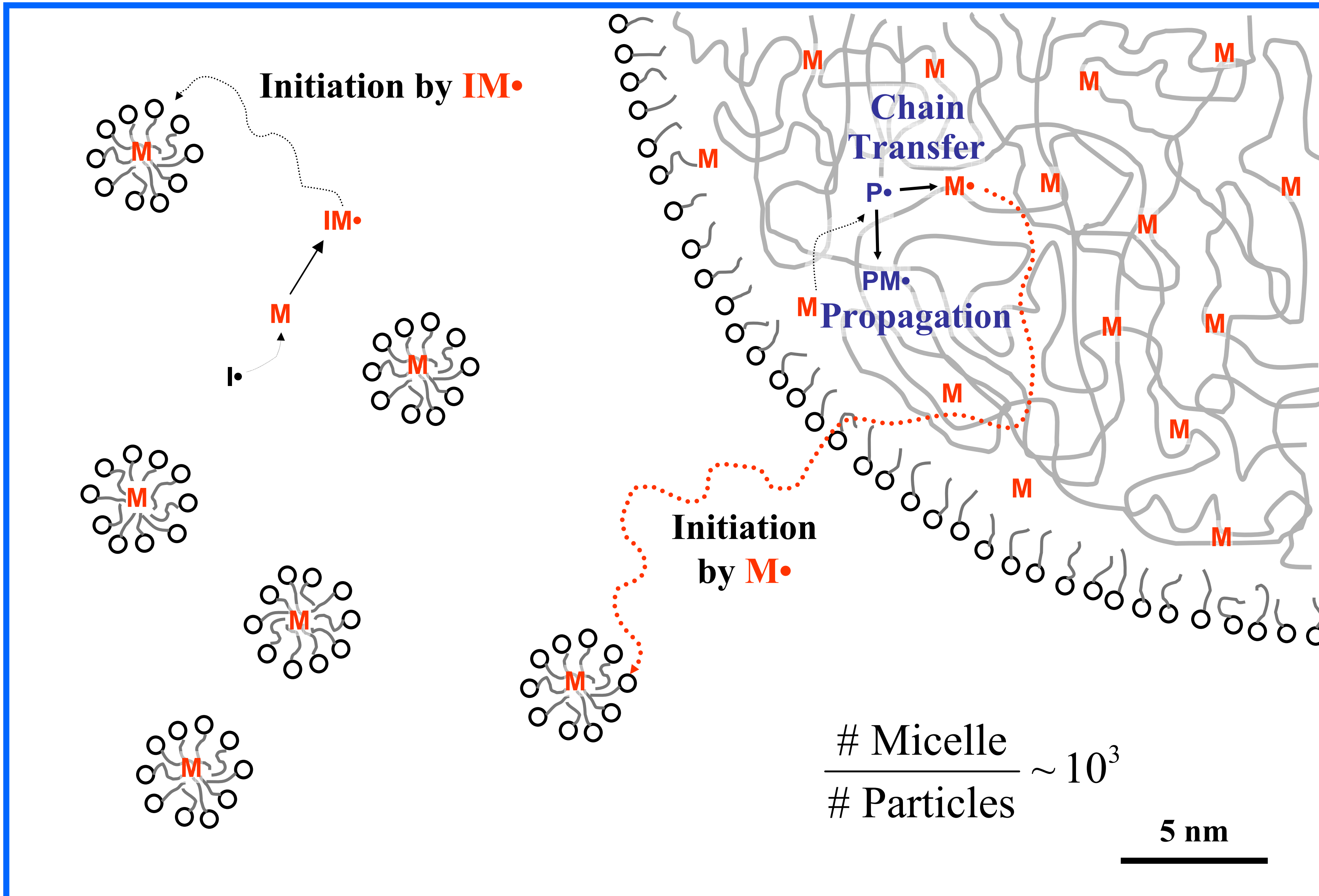
A Simple View Of Microemulsion Polymerization

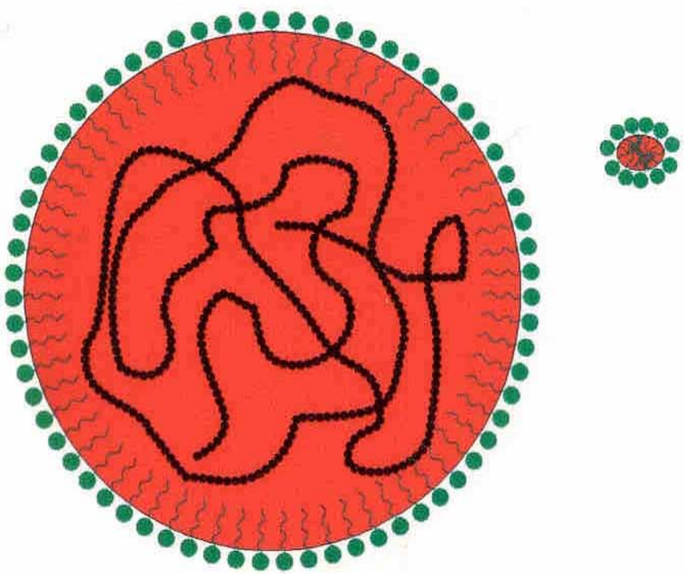


Kinetic Modeling: Monomer Concentration at Locus of Polymerization

At intermediate concentrations, which is closer to the truth?

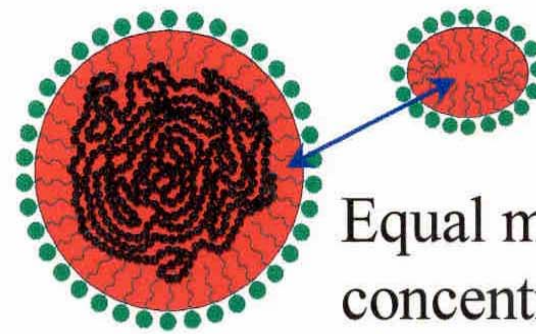
Monomer Swells Polymer	Monomer Does Not Swell Polyme

Monomer Swells Polymer



$$C_p \approx C_{max}(1 - f)$$

Monomer Does Not Swell Polyme



Equal monomer concentration

$$C_p \approx C_o(1 - f)$$

$C_o \Rightarrow$ Initial micelle core monomer concentration

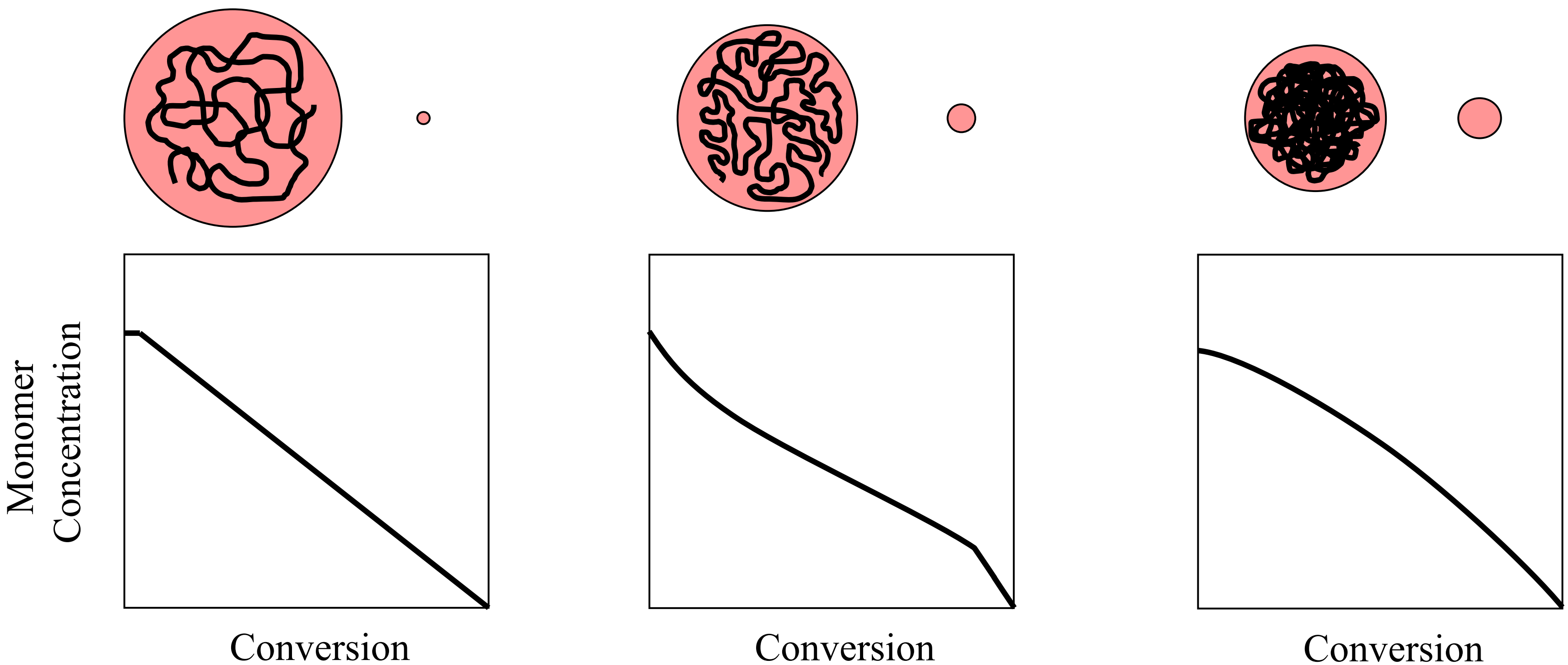
Carlos Co, Renko de Vries

How Does the Microstructure Evolve?

Case I
Flory-Huggins for both latex particles and micelles. All monomer is taken up by latex particles at ~ 5% conversion.

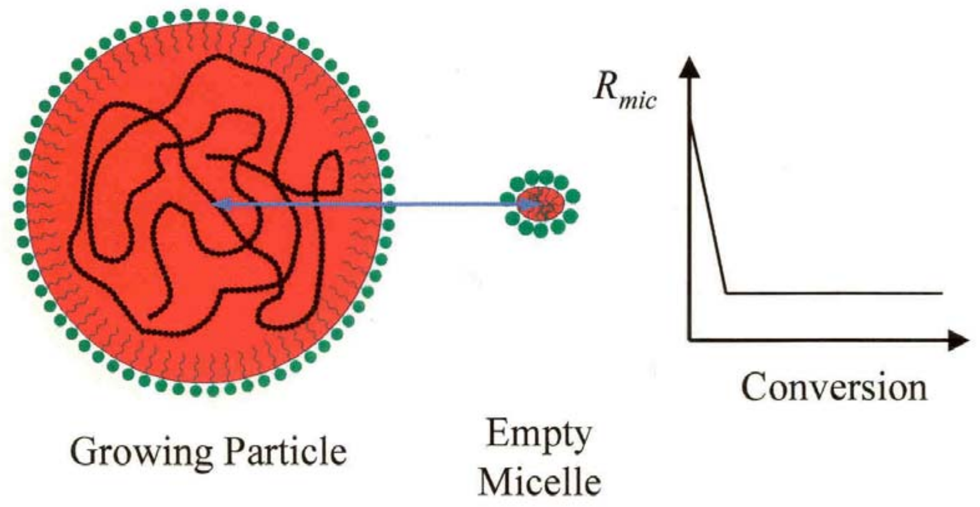
Case II
Flory-Huggins for latex particles and curvature energy for micelles. Monomer partitions between latex and micelles.

Case III
No swelling of polymer latex. Polymerization occurs in shell of latex particles with monomer concentration equal to that in the micelles.

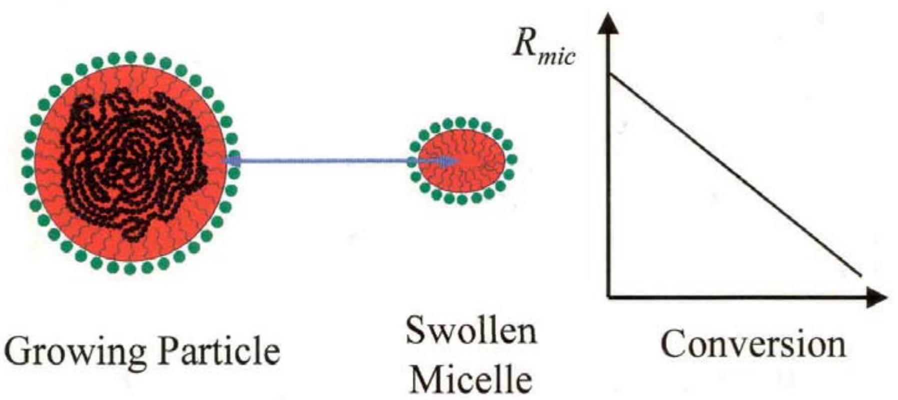


Monomer concentration is approximately linear with conversion.
Can differentiate only using Small Angle Neutron Scattering (SANS).

A) Swollen Chain

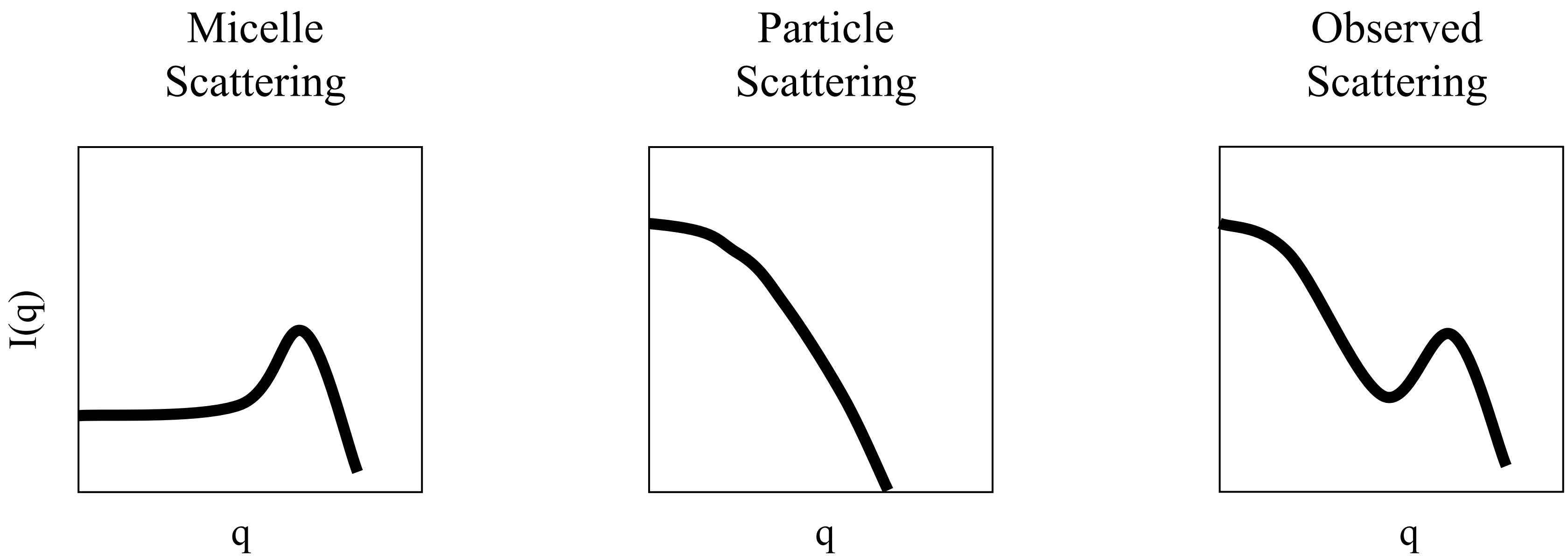


B) Compact Chain



Monomer Concentration at
Locus of Polymerization: $c = c_o(1\text{-}f)$

What Can SANS Tell Us?



How does the SANS spectra change as the microstructure evolves from micelles to a mixture of polymer particles and micelles?

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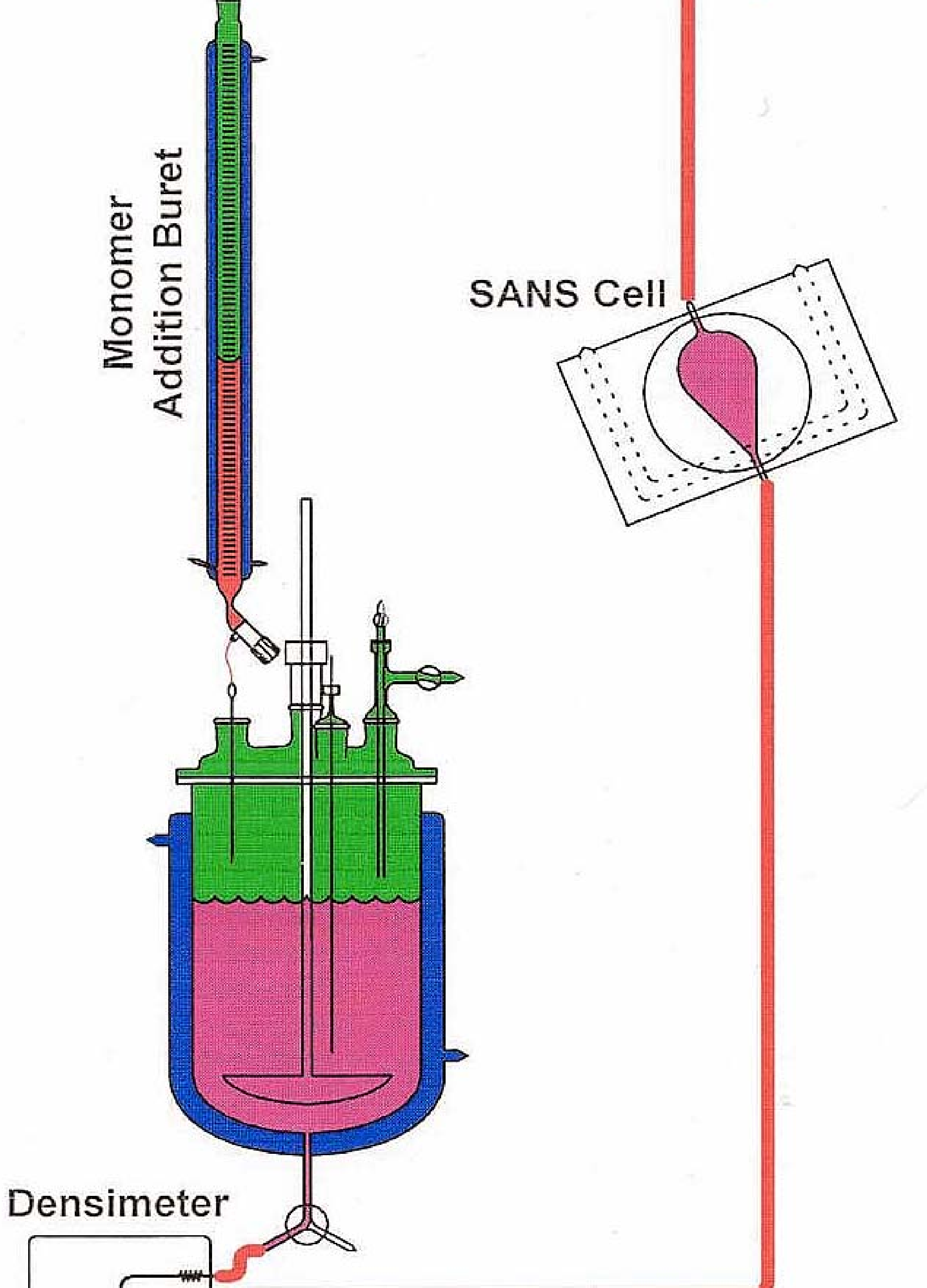
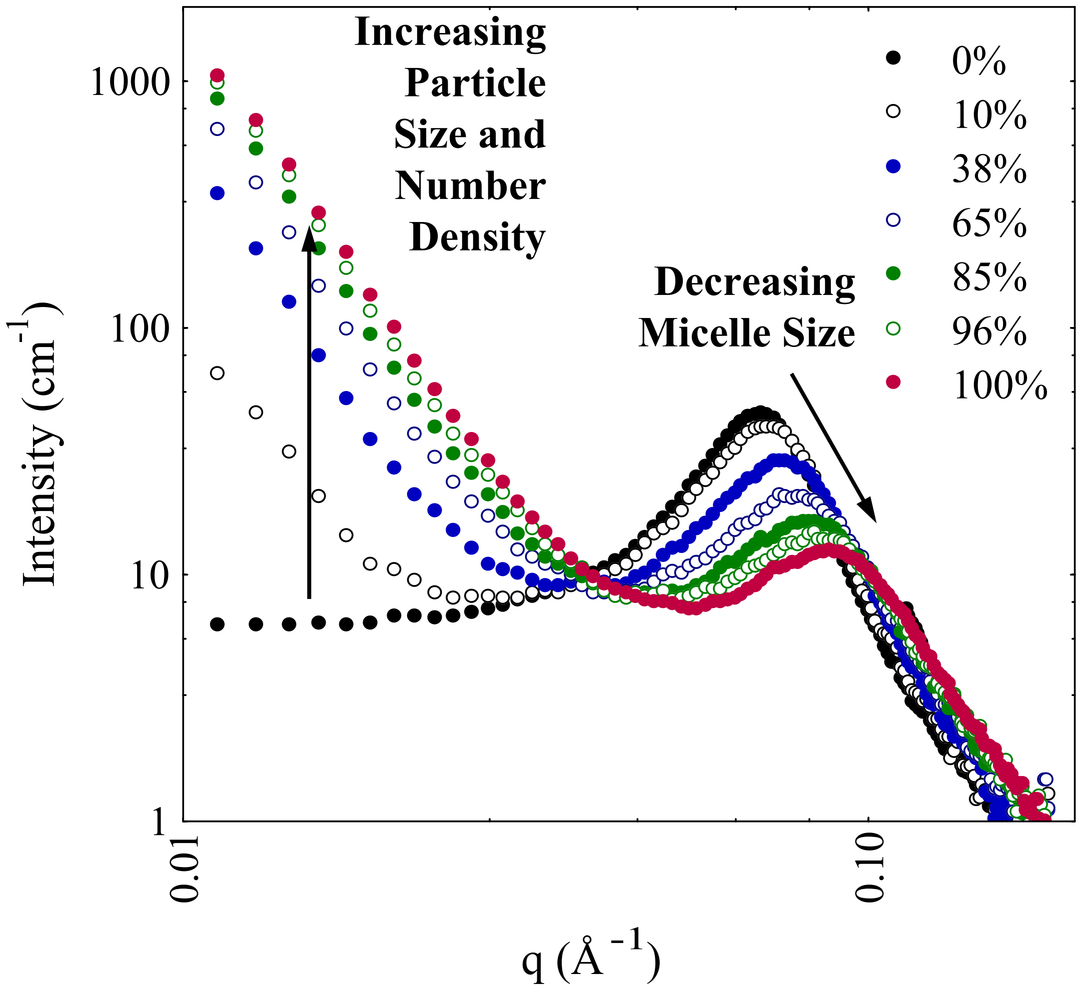
Reactor for Online Scattering During Polymerization



Online SANS / Kinetics Experiments

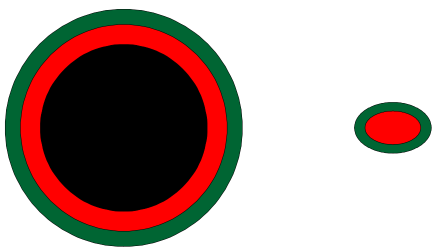
C6MA (DTAB/DDAB)



Gradual shifts in SANS spectra indicate that monomer partitions between the micelles and the polymer particles. Case I is incorrect.

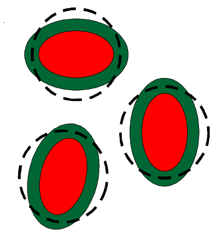
SANS Model for Online SANS Spectra

Form Factors

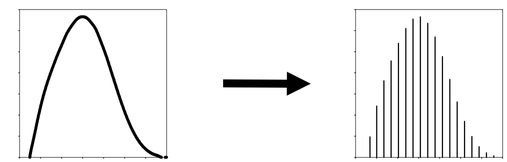


Polymer Micelle

Effective HS Interactions

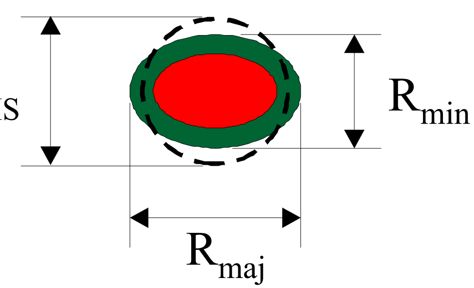


Discretize Model-Predicted Particle Size Distribution

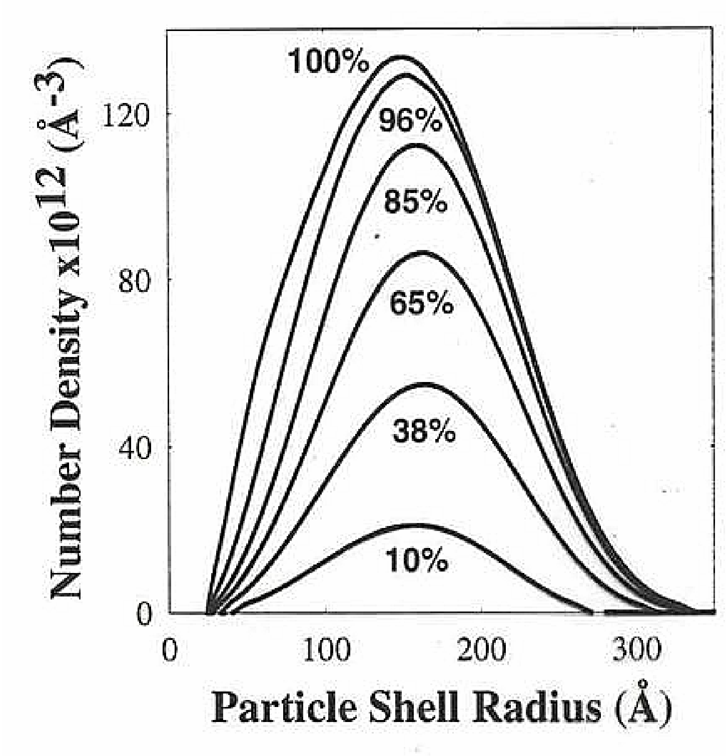


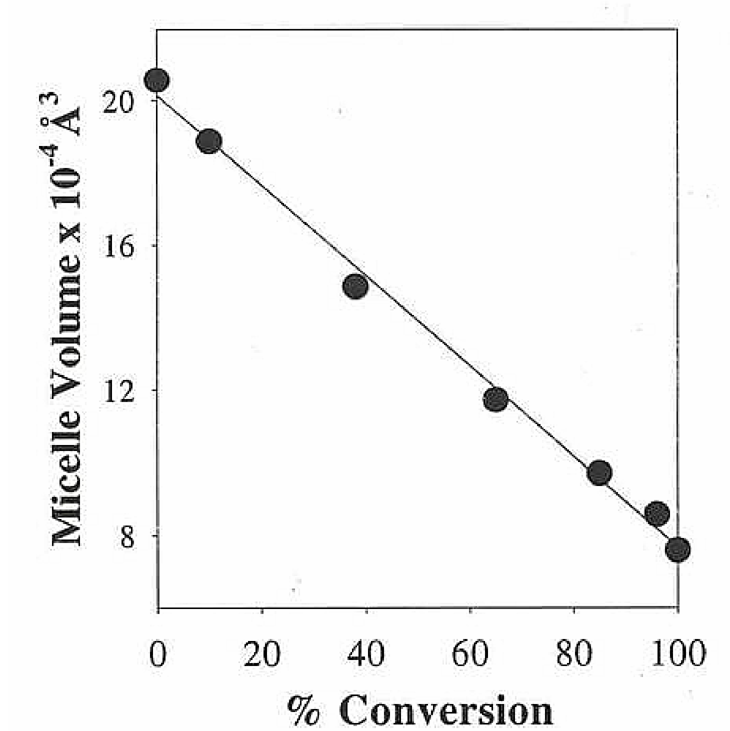
Calculate model intensities using Vrij's analytical equation

Three Adjustable Parameters



SANS Model Fitting Results





Particle size distribution model is consistent with SANS

Micelle size decreases steadily with increasing conversion

University of Delaware

Summary

- Free radical polymerization in and of complex fluids produces replicas
- SANS can record the dynamics of chemical transformations
- Faster physical transformations can be observed with stopped flow or other methods

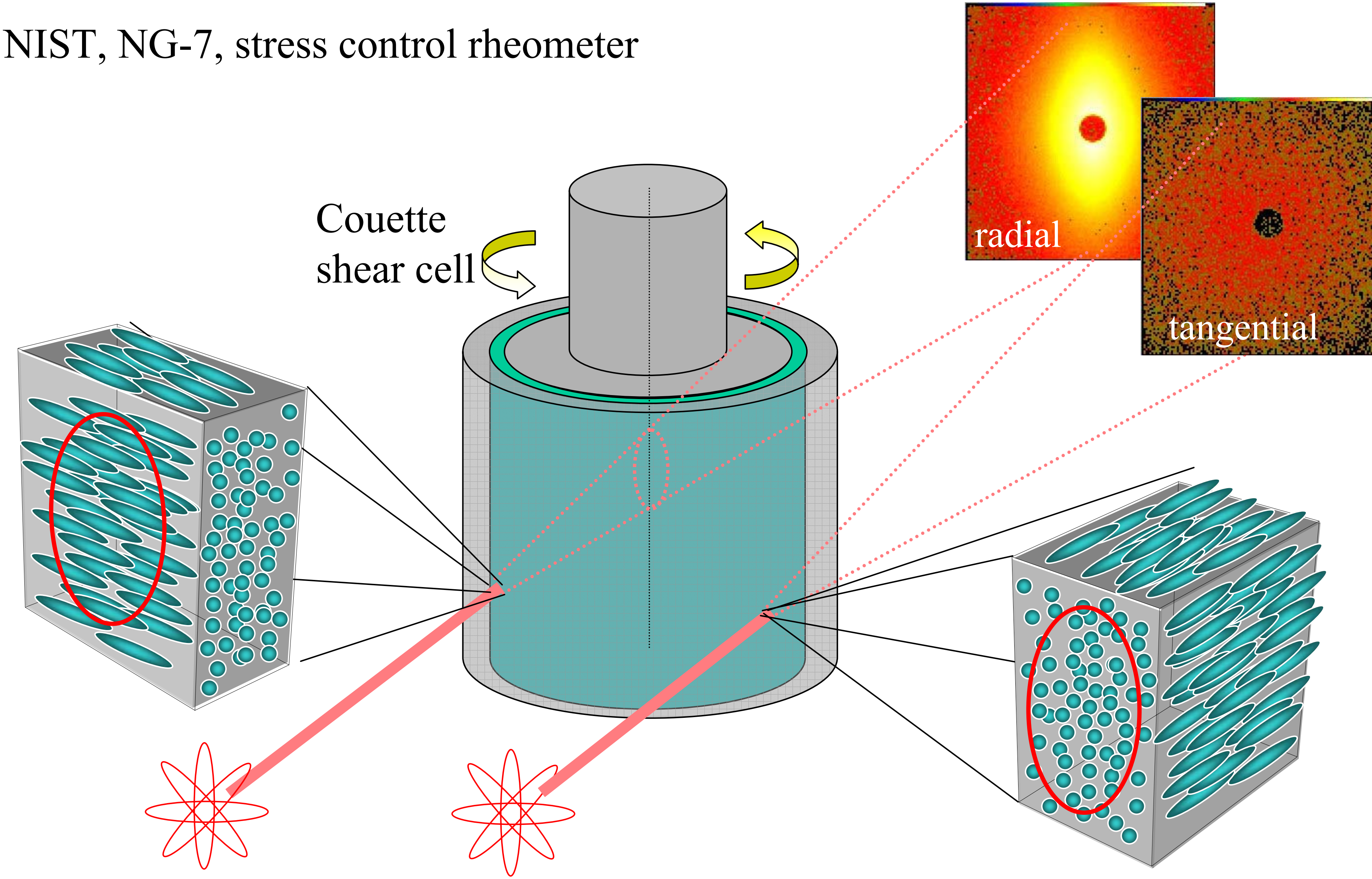
Rheology and SANS

- Structural information on complex fluids in the size range 1nm~1 micron both at rest and under **flow** conditions
- Access to **rheological** properties not accessible in a mechanical rheometer
- Contrast matching in SANS enables probing individual **components** in a mixture
- Initial target – ordering in worm-like micellar solutions

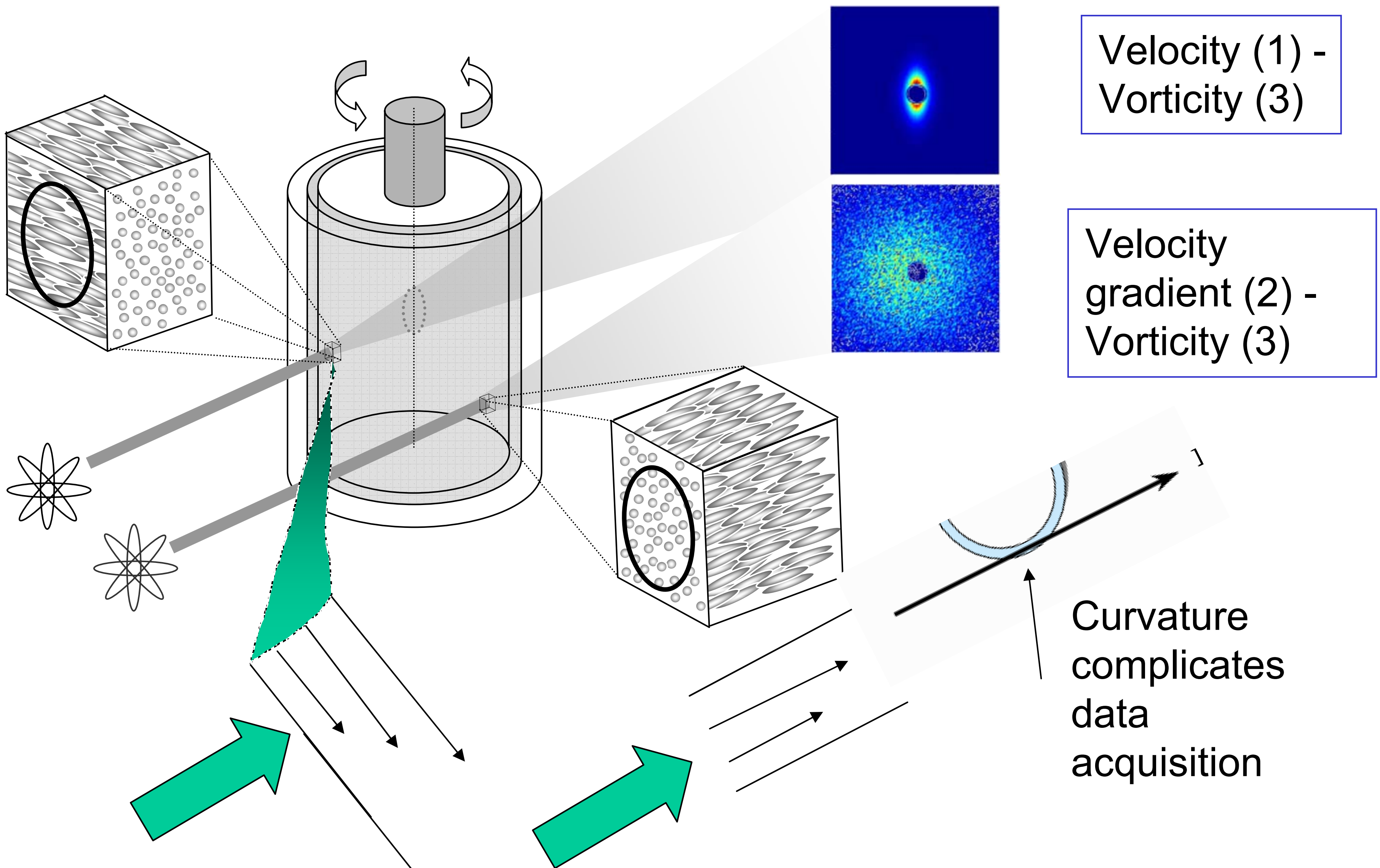
With Norm Wagner – University of Delaware

Rheo-SANS Investigation

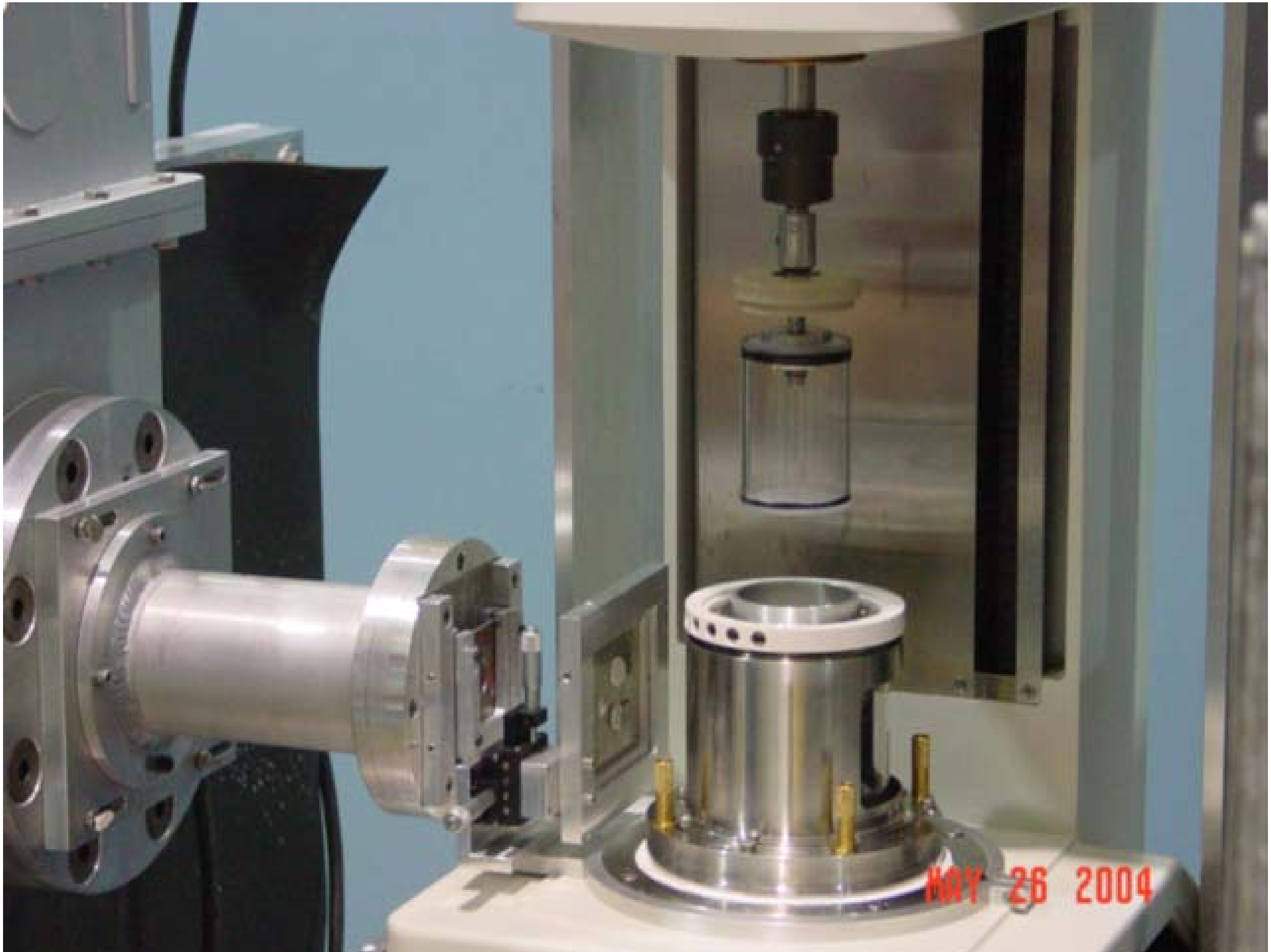
NIST, NG-7, stress control rheometer



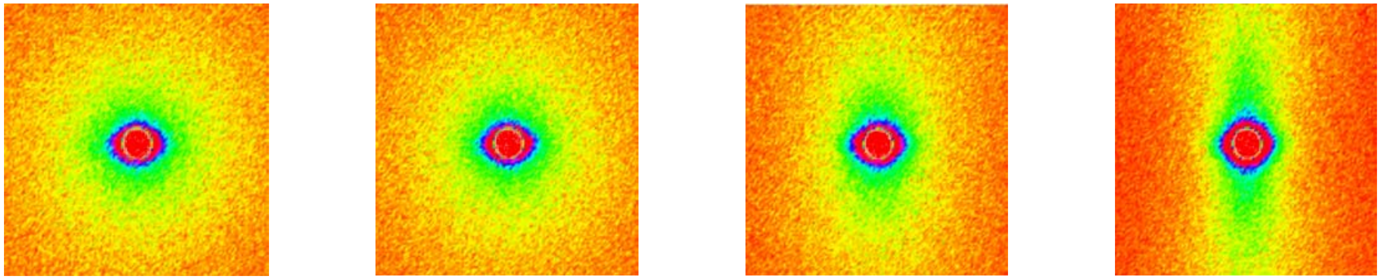
Current Rheo-SANS Geometries



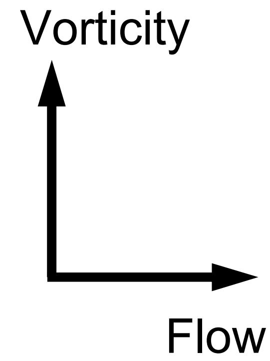
Rheo-SANS Couette Cell

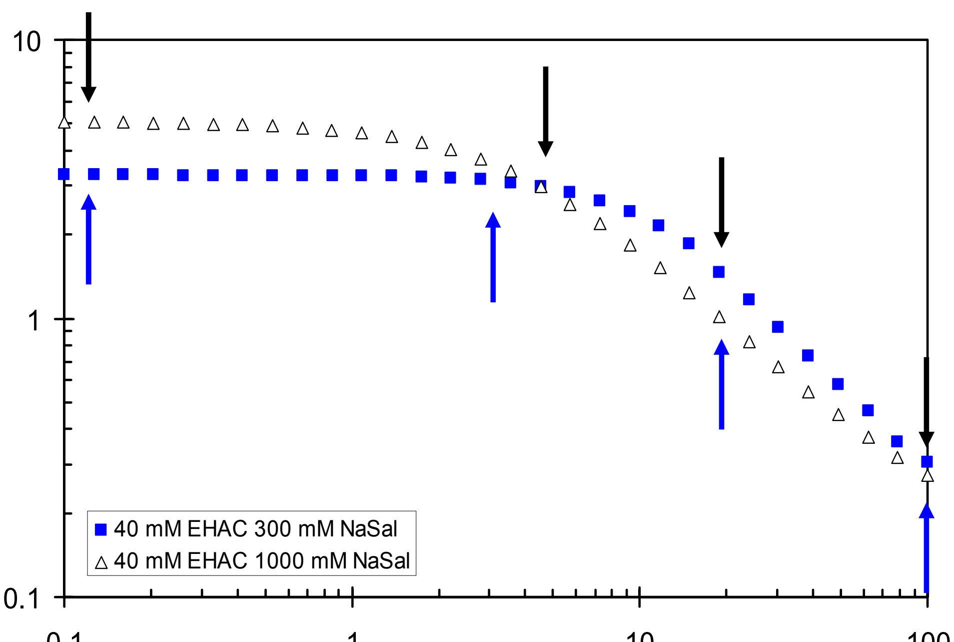


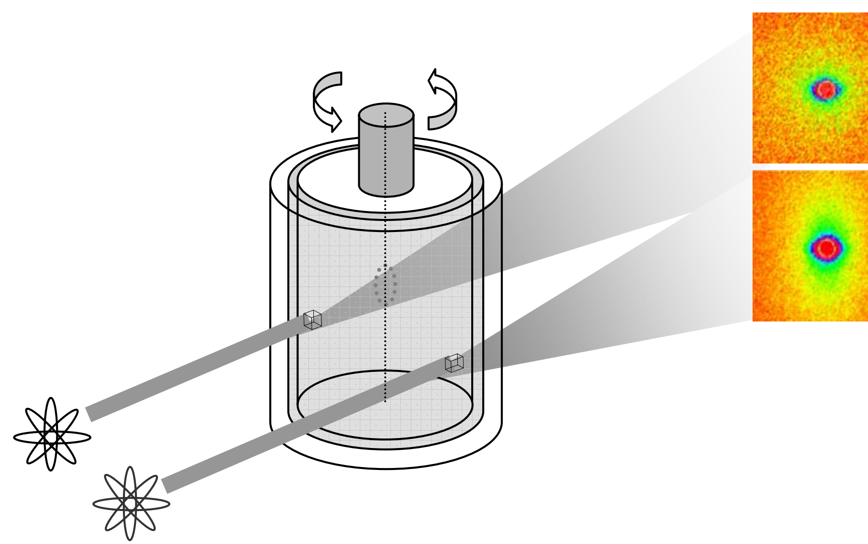
Rheo-SANS Comparison

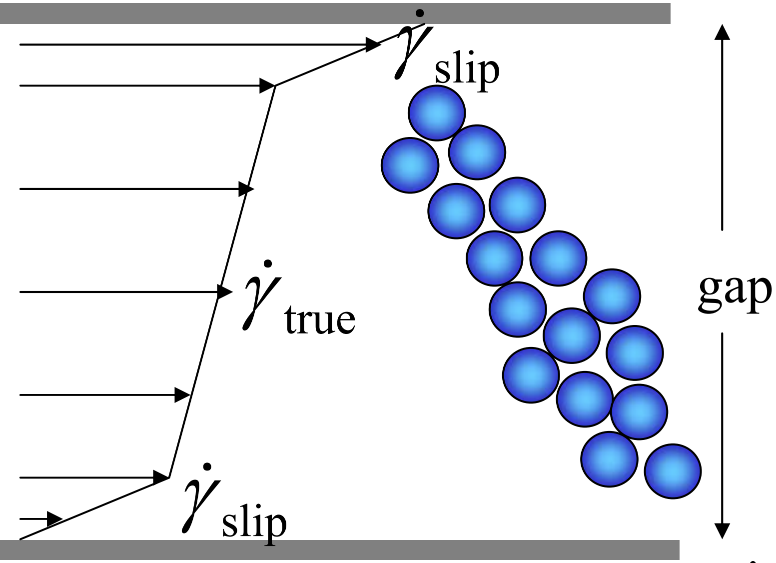


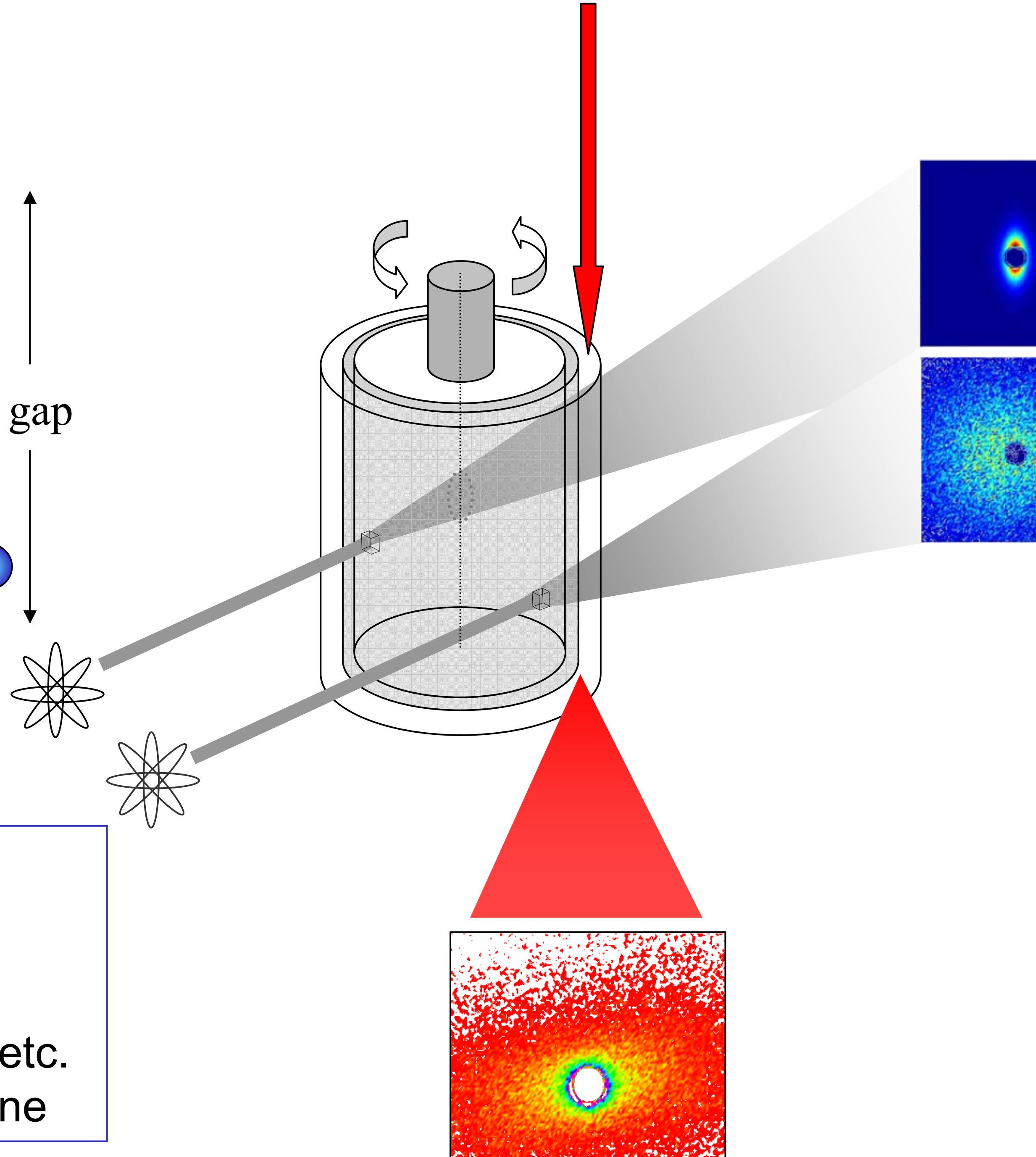
0.1 s^{-1} | 5 s^{-1} | 20 s^{-1} | 100 s^{-1}







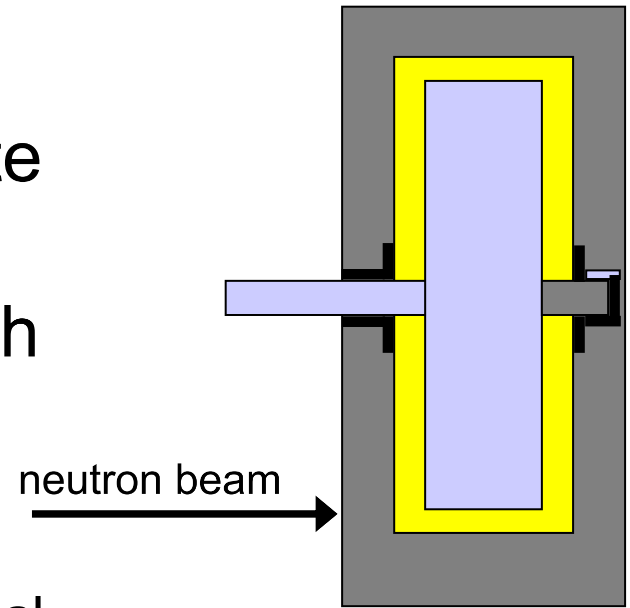


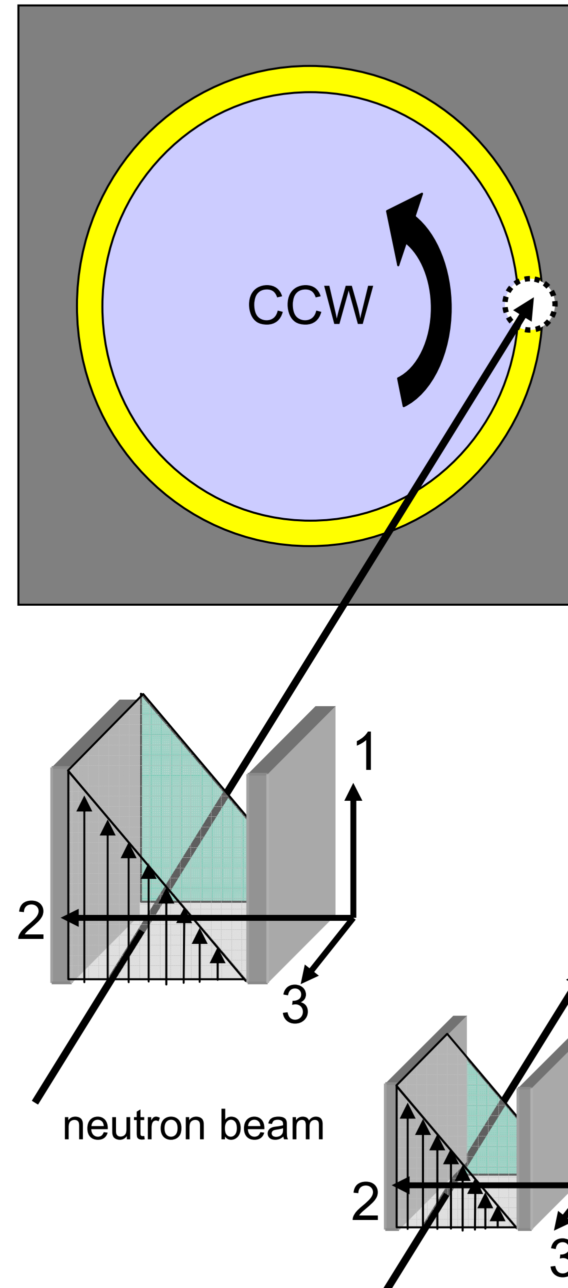


- Maximum microstructure deformation and alignment is available in the 1-2 plane
- Shear banding, wall effects, etc. are accessible only in 1-2 plane

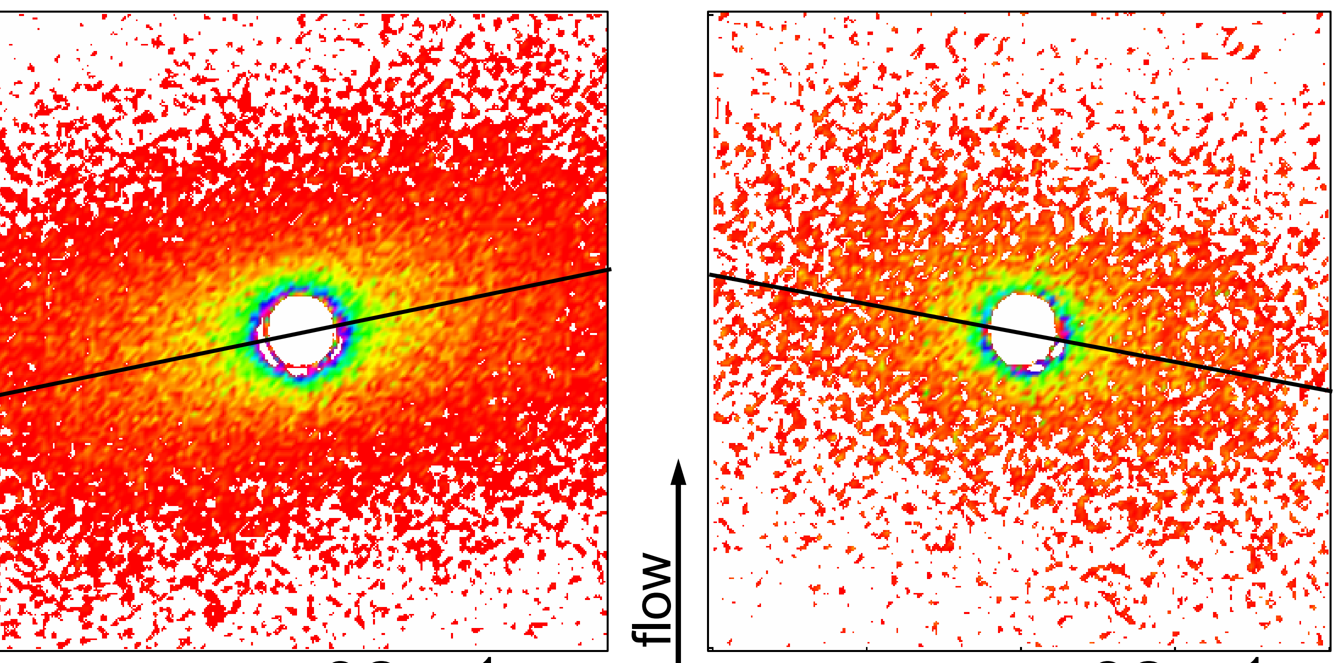
1-2 Plane SANS Setup

- Aluminum Couette
- 2.0 mm gap
- 10 mm path length





40 mM EHAC 300 mM NaSal

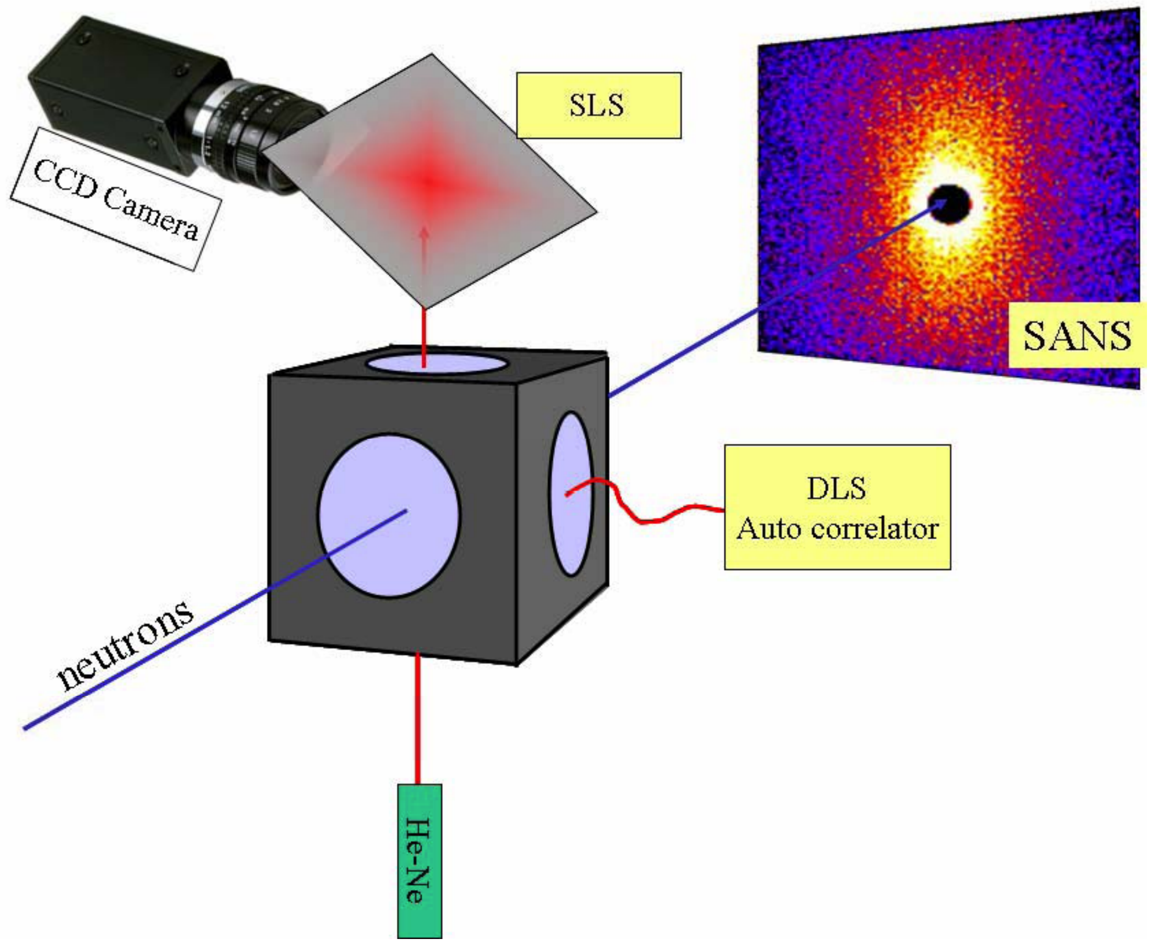


Summary

- Dynamics of self-assembled materials under flow can be resolved

Limitations and Challenges

- Expanded length scales
  - Lower q to see aggregation, etc.
- Dynamics needs time resolution
  - Chemical kinetics
  - Physical relaxations
- Diffusion processes (reptation!)
- External fields
  - $\underline{E}$, $\underline{H}$, $\underline{v}$, p, μ,…
- Biology!

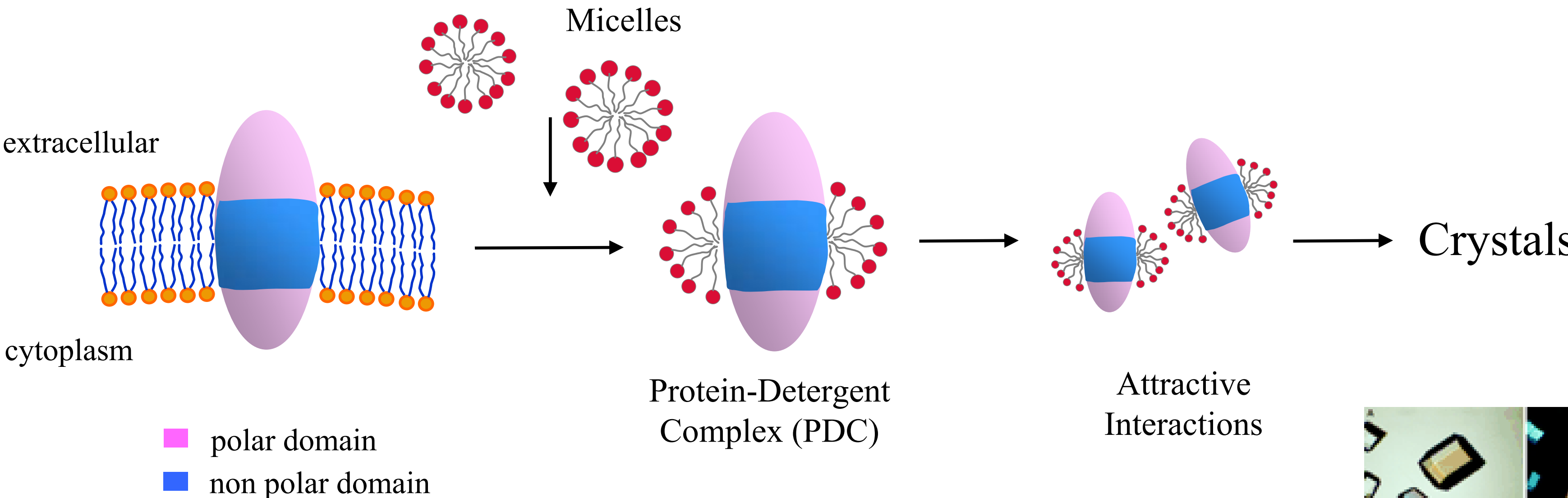


Simultaneously:

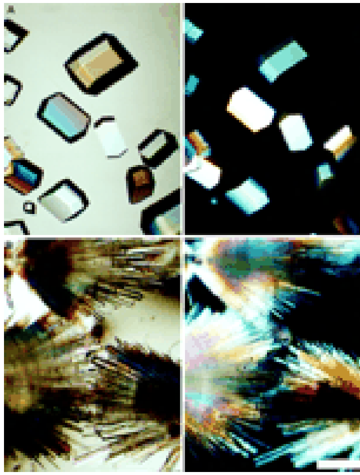
- small angle neutron scattering
- static light scattering
- fiber-optic directed dynamic light scattering

Biological Issues

- Protein configuration and interactions with lipids in native environments



- Protein function
- Proteins in action!



Needs

- Flux, Flux, Flux

Needs

Useable

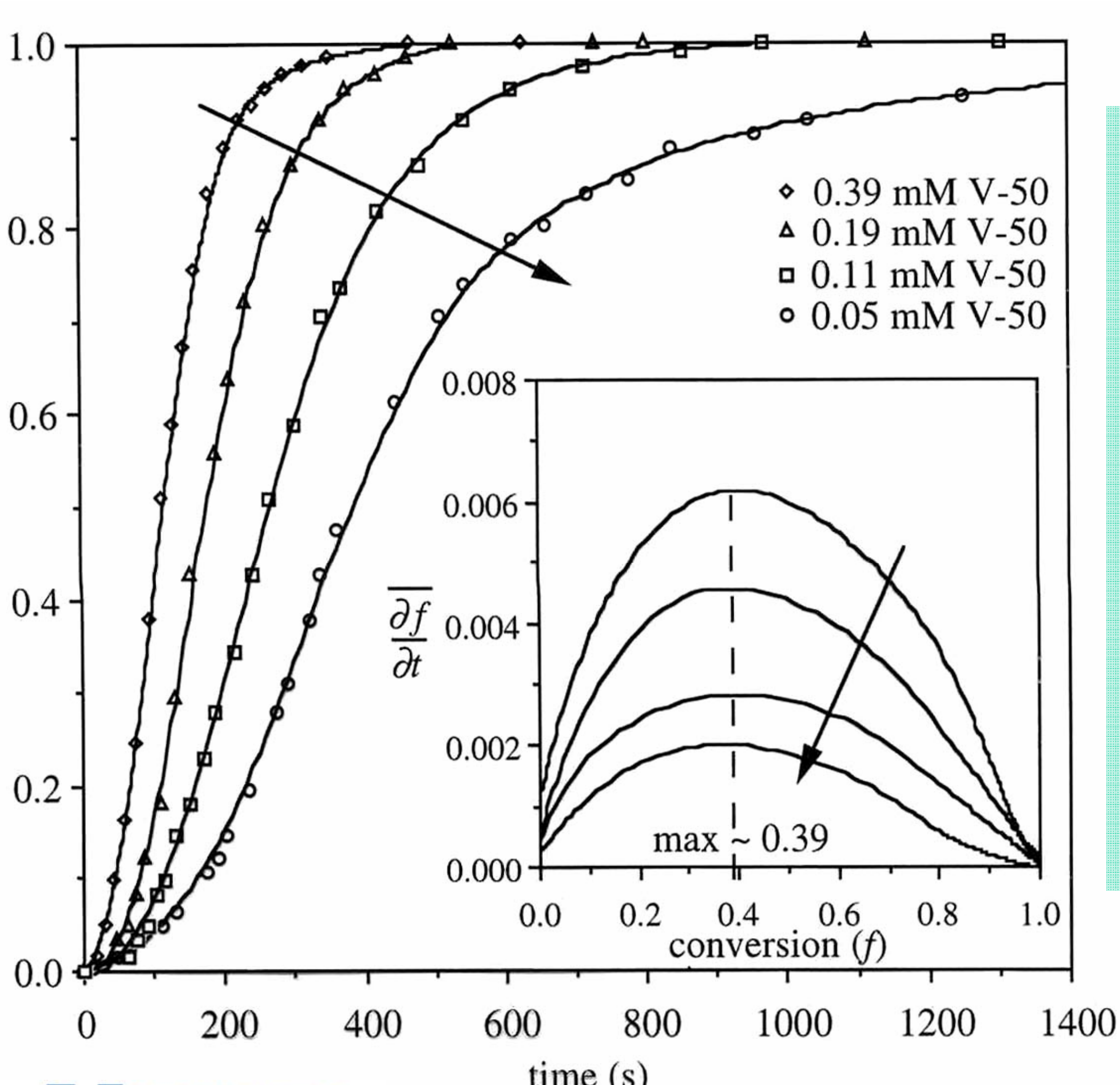
- Flux, Flux, Flux

Needs

Useable

- Flux, Flux, Flux
- Resolution
- But *useable* means
  - Better detectors
  - Better sample environments and sample throughput
  - Data analysis
    - Theory!

V – 50 Polymerizations



1. Rapid polymerizatio
2. 100% conversions
3. Rate profile paraboli
4. Average maximum rate at about **39%** conversion

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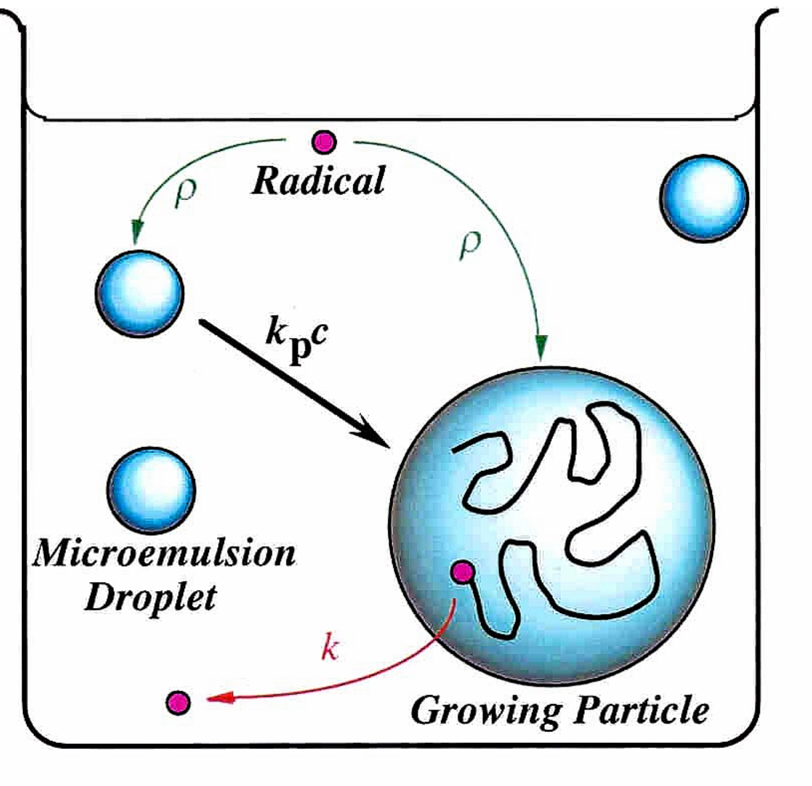
Microemulsion Polymerization – John Morgan



Initiation: $\text{I-I} \xrightarrow{k_d} 2\text{I}^\bullet$

Propagation: $\text{I}^\bullet + \text{M} \longrightarrow \text{IM}^\bullet \xrightarrow{k_p} \text{IM}_n$

Transfer: $\text{IM}_n^\bullet + \text{M} \xrightarrow{k_{tr}} \text{IM}_n + \text{M}^\bullet$

Combination: $\text{IM}_n^\bullet + \text{IM}_m^\bullet \xrightarrow{k_t} \text{IM}_{n+m}\text{I}$

Modeling the V-50 Rate Curves

- Fundamental rate equation for addition polymerization:

  c = monomer concentration at polymerization locus

  $[R^\bullet]$ = concentration of propagating radicals

$$-\frac{\partial c}{\partial t} = k_p [R^\bullet] c$$

- Microemulsion conversion form:

$$\frac{\partial f}{\partial t} = \frac{k_\mathrm{p} N^*(t) c(f)}{M_\mathrm{o}}$$

M_o = monomer concentration at polymerization locus (M)

N^* = propagating radical concentration in whole microemulsion (M)

Modeling the V-50 Rate Curves (cont.)

- Assumption: Monomer concentration within polymer particles given by:

$$c = c_o\,(1 - f)$$

c_o = initial concentration of monomer, M

- Entry rate is constant; all radicals remain active

$$N^*(t) = \rho_o t$$

ρ_o = rate of radical entry, M s^{-1}

Modeling the V-50 Rate Curves (cont.)

- Rate Equation: $$\frac{\partial f}{\partial t} = \frac{k_{\mathrm{p}} N^{*}(t) c(f)}{M_{\mathrm{o}}} = \frac{k_{\mathrm{p}} c_o \rho_o}{M_{\mathrm{o}}} t(1-f)$$

Or $$\boxed{\frac{\partial f}{\partial t} = At(1-f)}$$

Parameter: $$A = \frac{k_p c_o \rho_o}{M_o}$$

Conversion: $$\boxed{f = 1 - \exp\left(-\frac{1}{2} A t^2\right)}$$

Modeling Implications

Rate Maximum : $\overline{f'} = \sqrt{\dfrac{A}{e}}$

Conversion at Maximum Rate : $\overline{f} = 1 - e^{-0.5} = 0.39$

Time of Maximum Rate : $\bar{t} = A^{-1/2}$

- Dependence on Initiator Concentration:

Assume $\rho_o = 2k_d\,[I]$

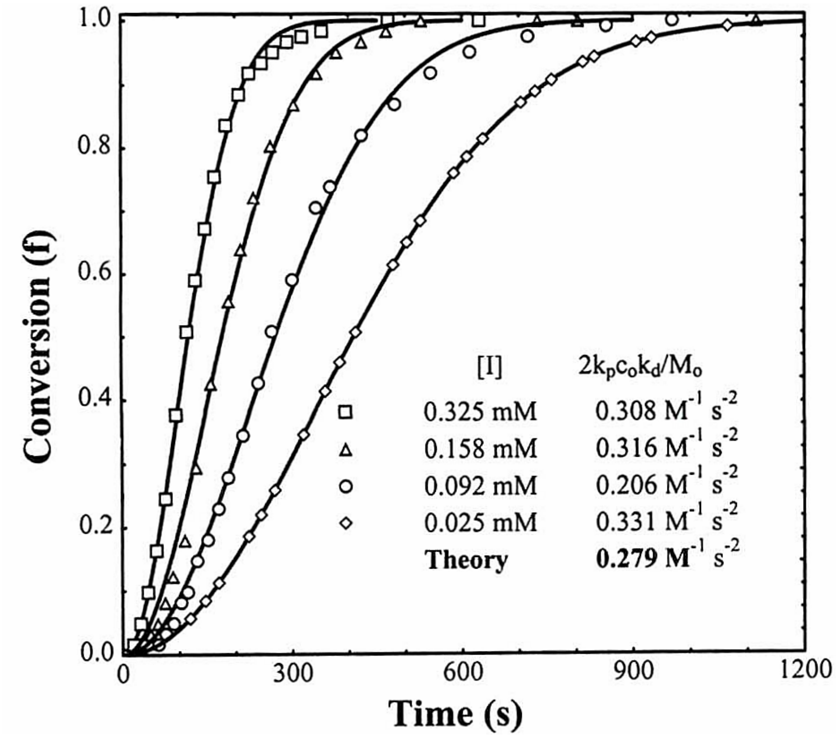
then A goes as [I]

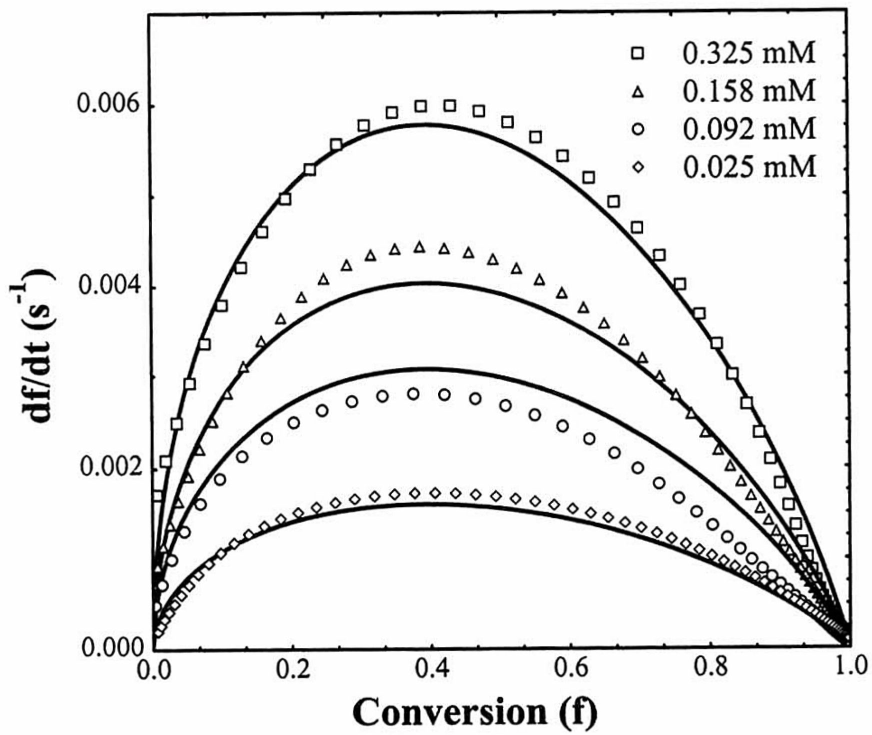
Measured Rate Constants

- Propagation Rate Constant
  - $k_p = 995\ M^{-1}s^{-1}$ (Pulsed Laser Polymerization)
- Initiator Decomposition Rate Constant
  - $k_d = 3 \times 10^{-5}\ M^{-1}s^{-1}$ (Literature)
- Initial Monomer Concentration in Droplet
  - $C_0 = 1.0\ M$ (SANS)
- Initial Monomer Concentration in microemulsion
  - $M_0 = 0.257$ (Formulation)

N.B. No fitted parameters!

Comparison with Experiment





Quantitative Agreement Through to Full Conversion